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Interface Imaging by Scanning Internal Photoemission

Abstract: A scanning internal photoemission (SIP) technique is used to obtain a high resolution map or image of the potential energy barrier at an insulator interface. The image is produced by displaying the internal photocurrent produced by a monochromatic beam of light scanned across the sample. A special technique was developed for focusing the light to a spot less than one micrometer in diameter. Photoemission images of a Si-SiO_2 interface "stained" with a fractional monolayer of sodium are presented along with photoemission and reflectivity images of a Nb_2O_5-Bi interface. These SIP images show inhomogeneities related to structural variations, impurities, and defects at the interface that previously were inaccessible to observation.

Introduction

Many methods are available for obtaining microscopic images of material surfaces, but surprisingly little has been done in the past to develop new techniques for viewing interfaces between materials. Scanning internal photoemission (SIP) is a recently developed technique [1–3] for probing interfaces with a light beam to produce a direct microscopic image (map) of an interface contact barrier. This paper presents a new high-resolution SIP measurement technique in which the image of a contact barrier is formed on a cathode ray tube (CRT) screen by intensity modulation of the beam.

Maps produced by the SIP measurement display the lateral inhomogeneities along a two-dimensional dielectric interface. This display allows a photograph to be made of the microscopic electronic structure of the interface, which has previously been inaccessible to observation. The technique is somewhat analogous to scanning electron microscopy (SEM), except that in this case a light beam is used to excite electron emission into a dielectric. Since the photoemission current increases rapidly as the electronic barrier at the interface is reduced, particularly for photon energies near threshold, local variations in the barrier are detected sensitively in the measured photocurrent. As in the SEM technique, the emitted current is displayed on a CRT screen as a function of the beam position to produce an image of the interface. The SIP images reproduced in this paper exhibit striking local inhomogeneities that are related to structural variations, impurities, and defects at the interface.

Physical basis of SIP technique

The success of the scanning internal photoemission technique depends on the sensitivity of the photocurrent near threshold to small variations in the interface contact barrier. Photocurrent produced by a scanning spot of light changes considerably as the beam moves over a surface which has a slightly nonuniform contact barrier. For a metal-insulator system near threshold, the photoyield is [4]

$$y = \eta(\hbar\omega - \Phi)^2, \tag{1}$$

where η is an efficiency factor and Φ is the photoelectric threshold. The fractional change in photoyield y or photocurrent i is

$$\frac{\Delta y}{y} = \frac{\Delta i}{i} = -\frac{2\Delta\Phi}{\hbar\omega - \Phi_0}, \tag{2}$$

which becomes quite sensitive to $\Delta\Phi$ as the photon energy $\hbar\omega \to \Phi$. As one might expect, the highest contrast is obtained with light that is slightly above the initial threshold Φ_0.

The spatial resolution of SIP, limited by the wavelength of the light beam, is on the order of a micrometer. This is sufficient to resolve many of the structural variations and defects that occur at a typical interface. The resolution of SIP could be further improved by a deconvolution technique [5], but our preliminary measurements indicate that little would be gained by a two-fold increase in resolution. To obtain a reasonable signal-to-

noise ratio in the photocurrent from a resolution-limited light spot, it was necessary to use laser radiation [3], which can be focused onto a nearly diffraction-limited scanning light spot. A power level of about 10^8 W/cm^2 produced a measurable photocurrent from the resolution-limited spot without thermally damaging the sample. This power level is sufficient to produce an image of a specimen 250 μm × 250 μm in less than ten minutes.

The SIP technique has been used to study several dielectric interfaces, such as Si-SiO_2 and Nb_2O_5-Bi. Although the Si-SiO_2 interface is almost uniform in the absence of impurities, a small amount of sodium ion coverage on the interface reduces the contact barrier in localized areas [1]. The dielectric strength of SiO_2 films is reduced in those areas where the contact barrier is lowered by the presence of sodium [2], a common impurity in this system. A uniform layer of sodium electrolytically deposited onto a clean interface was found to "decorate," or accumulate at, certain types of interface defects that can be viewed directly by SIP measurements. In effect, the deposited sodium "stains" defects such as microscratches, growth steps, and microcracks on the interface so that they can be detected directly in an SIP image. Interface microstructure, which is inaccessible to observation with other techniques, can be observed directly by SIP in conjunction with the sodium staining technique.

In the Nb_2O_5-Bi system, nonuniformities have been found in pure, uncontaminated specimens. Here, variations in the contact barrier are the result of a chemical reaction that takes place at the interface. Surprisingly, SIP has shown that many metal-insulator systems (e.g., Al-Al_2O_3, Cr-SiO_2, Nb_2O_5-Bi) display an inhomogeneous contact barrier quite unlike the simple, uniform barrier that was assumed in earlier work. It has become apparent that any study of metal-insulator interfaces can benefit from an investigation of the barrier on a local scale, because large-area measurements yield only averaged results on an inhomogeneous system. At its present state of development, the SIP technique seems well suited for investigation of dielectric interfaces on a scale of one micrometer or larger.

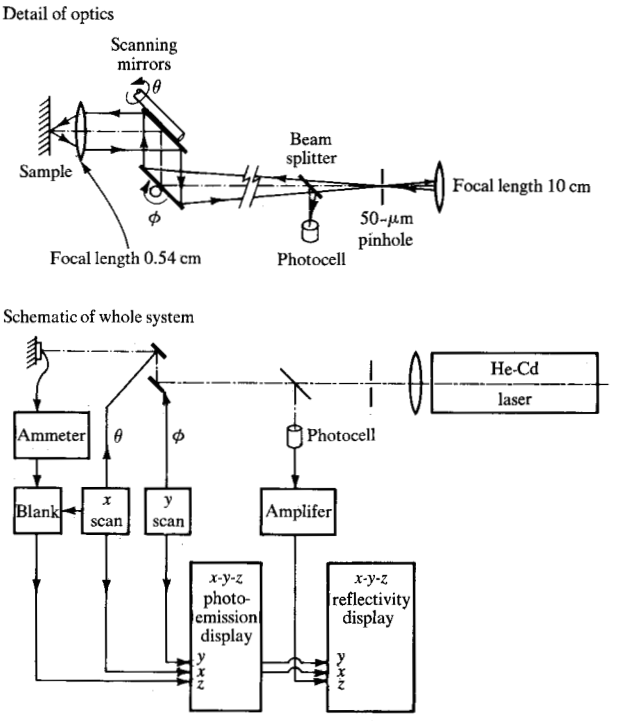


Figure 1 Optical system and measurement apparatus for the scanning internal photoemission (SIP) measurements. The system is brought to focus by adjusting the sample position to minimize the size of the light spot reflected onto the luminescent screen on the back of the 50-μm pinhole. The photocurrent produced by the scanning light spot is detected and displayed as a function of position on a CRT.

Measurement methods

A simple system with mechanically rotated mirrors was used to scan the light spot over a 250-μm-square area of the sample. The optical system is outlined schematically in Fig. 1. Radiation at 3250 Å from an RCA He-Cd laser was focused through a 50-μm pinhole to eliminate the light that diverged more than 0.5 mrad. Light from the pinhole was reflected from two front surface mirrors that rotate through the angles ϕ and θ. The focused spot of light from the objective lens scanned the sample as ϕ and θ were varied. For all values of ϕ and θ during the scan, the incident light filled the complete aperture of the lens. A spot velocity of 3000 μm/s on the sample was obtained with θ swept at 15 Hz and ϕ at 0.008 Hz.

The total spot size of about 0.43 μm is determined theoretically by two nearly equal factors—laser beam divergence and lens diffraction. Of course, the optical resolution deteriorates at points away from the center of the field because of the curvature of the lens focal plane. However, this degradation of resolution is barely discernable over a total field of 250 μm × 250 μm.

The problem of positioning and focusing the sample in the ultraviolet beam was solved by detecting the light reflected back from the sample. To understand this focusing technique, consider first the general linear system in Fig. 2(a). A point source on the object plane is focused onto a point in the image plane. Then, by time-reversal symmetry, any light radiated from the point at this image is focused back onto the point at the original object. If a reflecting surface is placed at the image, the configuration shown in Fig. 2(b) results. Light from a point source at the object is focused into a point on the reflector, which then reradiates the light back through the optical system. As before, light from a point on the

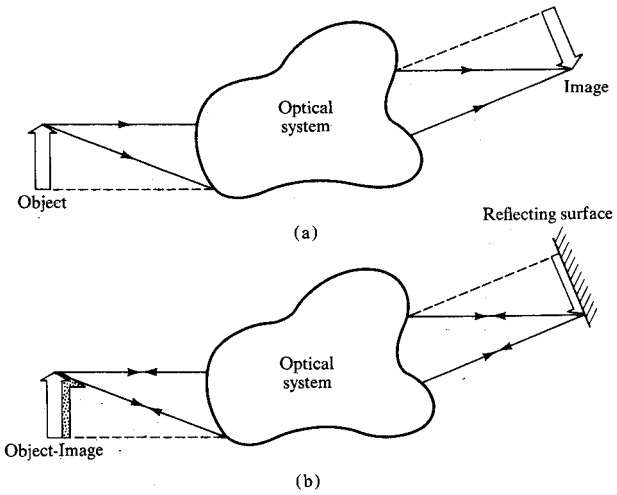


Figure 2 Schematic representation of the linear optical system outlining the time reversal principle: (a) Point object is brought to focus at the image position, and (b) reflecting surface at the image returns the light through the system back to the object point.

reflector is focused by the system onto the original object point. Light from the object point is returned to this same point only if the reflecting surface is in focus.

We use this principle to focus the system outlined in Fig. 1. Light from the pinhole is focused onto the sample, which then reflects part of the light back through the system. When the sample is in focus, the reflected light returns to the pinhole, independent of the mirror positions ϕ and θ. However, if the sample is out of focus, the reflected light strikes a fluorescent screen around the pinhole where it is seen as a disc of visible light. The system is brought into focus simply by adjusting the sample position until all of the reflected light is refocused back onto the pinhole.

To position the light spot on the sample, an image of the sample is obtained from the reflected light. Part of the light reflected from the sample is directed onto a photocell by a beam splitter, as shown in Fig. 1. The light falling on the photocell comes to focus at a position independent of mirror angles ϕ and θ. Current from the photocell, when displayed on an intensity-modulated CRT as a function of x and y, forms an image of the sample corresponding to its optical reflectivity at the wavelength of the source laser. This reflectivity image is essential for locating the sample in the beam and for examining the surface conditions of the sample during measurement.

Both the photocurrent and the light reflected from a sample are detected and displayed on CRT screens by circuitry shown schematically in Fig. 1. The two scanning mirrors are mounted on galvanometer movements which are driven by the nonsynchronous sawtooth generators x-scan and y-scan. These generators also drive the x and y axes on the CRT display. An image of the internal photoemission is formed on a CRT with z-axis modulation by the detected photocurrent from a Keithley 18000 picoammeter. The retrace scan is blanked by pulses from the x-scan generator. Images of z-axis-modulated CRT display of photocurrent are produced photographically. In a similar way, sample reflectivity is displayed on a CRT with z-axis modulation by the current from a photodetector that senses the reflected light. An advantage of this technique is that both the photoemission image and the reflectivity image appear on the same coordinate system, so that direct comparison between the two can easily be made.

Photoemission and reflectivity images

Photoemission and reflectivity images were obtained from Si-SiO_2 interfaces at $\lambda = 3250$ Å and from Nb_2O_5-Bi interfaces at $\lambda = 6328$ Å. In each case the SIP images show spatial inhomogeneities that can be related to physical structure.

Scanning internal photoemission maps shown in Figs. 3(a)–(c) each cover a field of about 250 μm × 250 μm and were obtained from a Si-SiO_2 interface on which sodium had been electrolytically deposited to an average density of 4×10^{12} atoms/cm^2. In each case the silicon substrate was doped with phosphorus to a density of 10^{20} atoms/cm^3. The sodium was initially distributed uniformly over the interface, as measured by radiographic techniques with a spatial resolution of about 50 μm [6]. After about 100 hours at 150 °C, the interface barrier was examined by SIP and found to be spatially nonuniform. It is known that the effect of sodium at the interface is to produce a monotonic increase in photoyield with increasing sodium ion concentration [7]. Therefore an SIP map of the interface reflects the inhomogeneous distribution of electrically active sodium on the Si-SiO_2 interface.

These SIP maps (Fig. 3) show the photocurrent as intensity vs x and y. The bright areas correspond to regions of high sodium ion concentration on the interface, because of the direct relationship between photoyield and concentration of active sodium. Each of the maps has several features in common; these include microscratches, sodium-rich spots of about 1-μm diameter, and dark regions of about 10-μm diameter. The resolution apparent in these SIP maps is more than an order of magnitude greater than that reported previously [1,3].

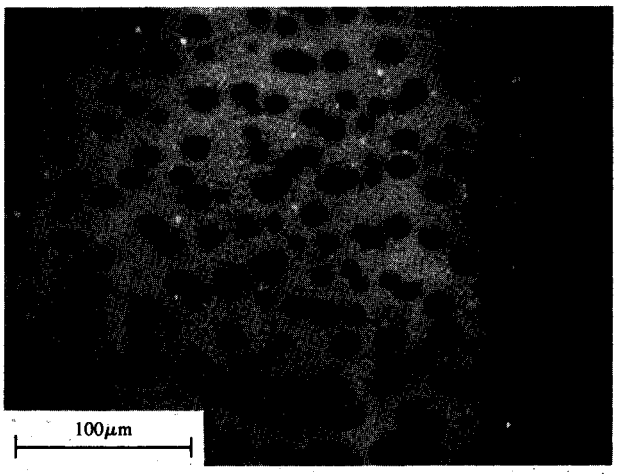
The microscratches, which are stained by excess sodium, are nearly straight lines several hundred micrometers long. These lines appear to be resolution-limited, with a width of 1 μm or less. There seems to be no relation between the line direction and the crystallographic

axes of the silicon, which has a (100) surface oriented such that the [110] axis is horizontal. It is interesting that such narrow interface microscratches can lead to local sodium along the scratches and to a subsequent degradation of the dielectric [2].

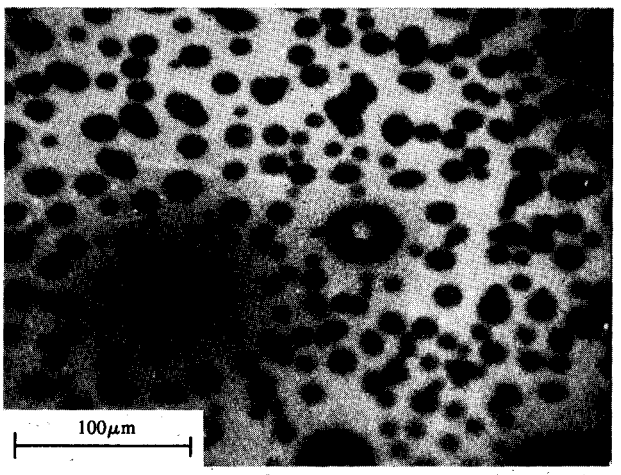
Another feature seen in the SIP maps is the dark spots about 10 μm in diameter. Spots like these were also found in other Si-SiO_2 interfaces on heavily phosphorus-doped silicon. Two reasonable explanations for the "Swiss cheese" pattern formed by these dark circular regions each involve the presence of local regions of high phosphorus concentration near the interface. Recent Auger measurements at SiO_2 layers on phosphorus-doped silicon indicate that a phosphorus-rich region exists in the SiO_2 very near the interface [8]. Thus the explanations are that either the sodium does not reach the interface in these areas because it is immobilized by a region of P_2O_5-SiO_2, or the sodium that does reach the interface is rendered ineffective by chemical combination with phosphorus very near the interface. However, full evidence linking phosphorus to the dark circles in the SIP maps has not yet been obtained. SIP measurements are being used to determine the influence of phosphorus concentration on the size of the dark circles as well as to investigate the possibility that the circles are related to something other than the presence of phosphorus.

A third and somewhat puzzling feature in the maps of Fig. 3 is the presence of small bright spots that are approximately the dimension of the resolution limit. The explanation for these spots is unknown at present. One can speculate that they are sodium that has naturally segregated into clusters due to a mechanism proposed by Williams and Woods [9]. However, the large, irregular spacing between the spots and the presence of uniform areas without spots suggest that the spots are associated with a defect or impurity in the sample itself. It is possible that microparticles introduced during processing of the wafers are responsible for the small spots of reduced contact barrier. The SIP technique promises to be fruitful in finding the explanation of this clustering. The questions raised about this and other features in the SIP maps are timely in that the answers will provide information about the physical structure of the extremely important Si-SiO_2 interface.

High contrast measurements are very effective in bringing out details in SIP maps. As an example, the map [Fig. 4(a)] of a Si-SiO_2 interface coated with sodium to a density of 4×10^{12} atoms/cm^2 includes a dark spot with a surrounding halo. The same area is shown on the high-contrast map in Fig. 4(b); the photocurrent signal was amplified and biased to remove the uniform background so that only the halo stands out above the background. In a similar way, the background photo-



(a)



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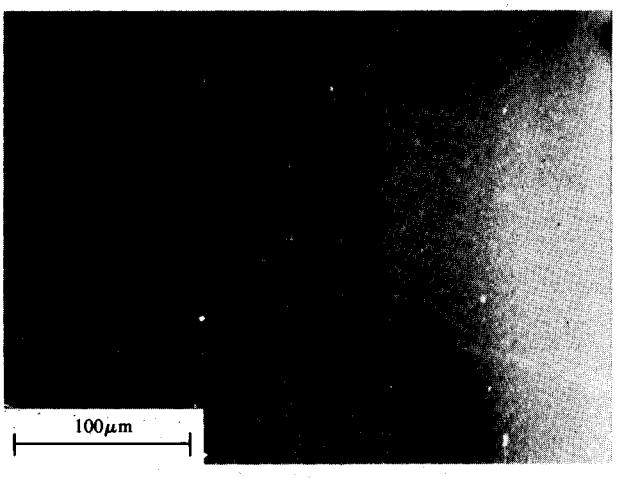
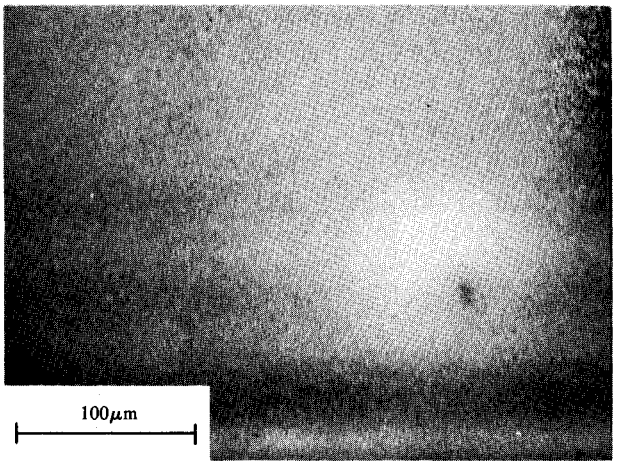
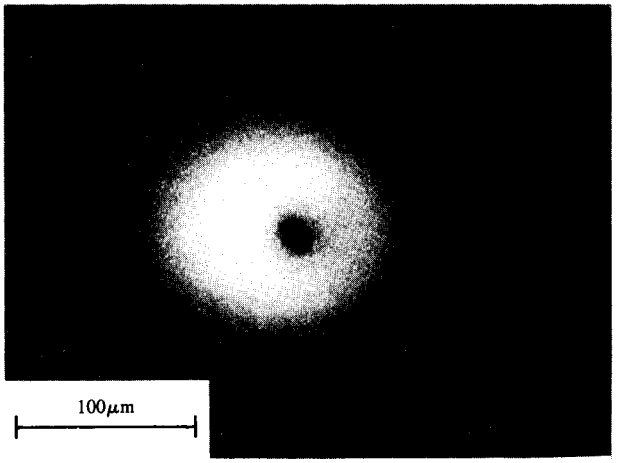


(c)

Figure 3 Scanning internal photoemission maps of three samples of a Si-SiO_2 interface covered with 4×10^{12} sodium atoms per square centimeter; measured with light at 3250 Å. The light areas indicate a high photoyield produced by the presence of sodium on the interface. The x and y axes are parallel, respectively, to the horizontal and vertical directions of these maps.

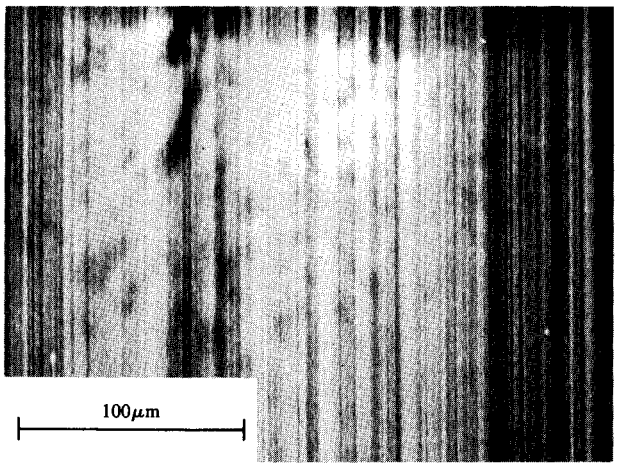


(a)

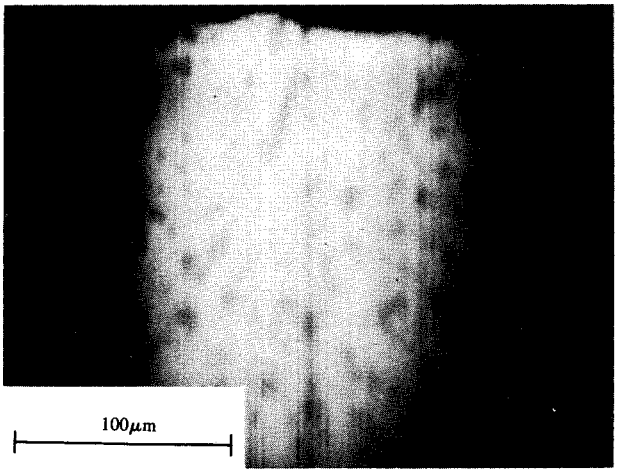


(b)

Figure 4 (a) Scanning internal photoemission map of a Si-SiO_2 interface covered with sodium at a density of 4×10^{12} atoms/cm^2; (b) high-contrast map of same area; measured with light at 3250 Å.



(a)



(b)

Figure 5 (a) Scanning internal photoemission map of a Nb_2O_5-Bi interface; (b) high-resolution reflectivity map of the same area; measured with light at 6328 Å.

emission can be removed from maps to reveal other structures such as microsplits [9] and microscratches of the silicon surface. Although microsplits are far too narrow to be resolved optically, they show up clearly as excess photocurrent in the SIP maps.

The SIP technique was also used to study metal-insulator interfaces such as that of Nb_2O_5-Bi; this interface is of interest because of the fast switching found in thin Nb_2O_5 films. In this case, photocurrent was emitted from a 200-Å-thick bismuth electrode into the Nb_2O_5 by a He-Ne laser [11]. The 1.96-eV He-Ne laser was substituted for the He-Cd laser so that the photon energy would be close to the photoemission threshold, where the sensitivity of the technique is greatest.

A representative SIP map [Fig. 5(a)] displays about 250 μm $\times$ 250 μm of the interface. Spotty dark regions in the map apparently result from a higher-than-average contact barrier. The vertical striations are produced by slow variations of the leakage current from the sample, which occurred throughout the slow scan in the horizontal direction. For a comparison, a high-contrast reflectivity map of the same area of the sample is shown in Fig. 5(b). The dark areas in the reflectivity coincide with the areas of high contact barrier. This sort of reflectivity variation is typical of a metal-dielectric system in which an interface reaction has taken place. The patchy barrier, which is characteristic of the Nb_2O_5-Bi system, is the subject of a more general study [12].

The value of the SIP technique is apparent from our investigations of the simple systems reported here. It is anticipated that SIP will be useful in studies of interface reactions, impurity segregation and diffusion on inter-

faces, and structural defects on semiconductor interfaces with other materials. In particular, defect studies on a Si-SiO_2 interface stained with mobile alkali ions will continue to be fruitful.

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